

The Degradation of Perfluorinated Organic Thin Film During XPS Measurement

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Although XPS is generally accepted as a non-destructive surface analysis technique, the degradation of organic materials was observed during XPS measurement. Several factors for sample damages during XPS measurement have been reported. In this study, we have focused on the photoelectrons generated from the substrates. Thus, the degradation of organic thin films made of 1H, 1H, 2H, 2H-perfluorodecanethiol (PFDT) and 1H,1H,2H,2H-perfluorodecyltriethoxysilane (PFDS) on metal plates (Au, Ag, Cu, Ni, Mo) and silicon wafer were evaluated in order to investigate the influence of photoelectrons on the degradation of those thin films. F 1s peak intensities of both PFDT and PFDS films decreased during XPS measurement and the degradation rates obeyed first-order reaction. The order of damaging factor, β was Au>Cu> Ni> Ag>Mo>Si, and the β increased with the area of wide spectrum from 0 to 1450 eV (kinetic energy; 36 to 1487 eV). As the area is assumed to be proportional to total photoelectrons generated inside the sample, it was concluded that the photoelectrons from the sample itself affects the sample damage during XPS measurement.

INTRODUCTION

There are many techniques to analyze solid surfaces by means of detecting electrons and light emitted by the irradiation of probing beams. XPS is generally accepted as a non-destructive surface analysis technique. However, the surface damages have been observed during XPS measurement for many materials, such as polymers^[1-9], Lamgmuir-Blodgett^[10-12] films, organosilane^[13,14] and alkanethiol^[15] monolayers on solid substrates and some metal oxides^[16,17].

Factors for the surface damage are considered to be X-rays, heat radiation from filament, photoelectrons generated from the sample itself, and electron beam from Al filter, etc. Among these factors, we focused on the photoelectrons generated from the sample itself. Thus, the degradation of organic thin films made of 1H, 1H, 2H, 2H-perfluorodecanethiol (PFDT) and 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane (PFDS) on metal plates (Au, Ag, Cu, Ni, Mo) and silicon wafer were evaluated in order to investigate the influence of

photoelectrons on the degradation of perfluorinated organic thin film during XPS measurements.

EXPERIMENTAL

Materials and preparation of perfluorinated organic thin film

As the surface modification reagents, PFDT (Oakwood Products) and PFDS (Wako chemicals) were used without further purification. Five kinds of metal plates (Au, Ag, Cu, Ni, and Mo) and Si wafer were used as solid substrates. Each plate was ground by alumina abrasive paper. Then Au, Ag and Cu plates were cleaned with Ar ion sputtering until no evidence for contamination (C 1s and O 1s peaks) were confirmed in XPS chamber. Si wafer was cleaned according to RCA cleaning procedure; boiling in the solution mixture with the ratio,

pure water: 30% H_2O_2 : 25% NH_3OH = 6:1:1.

Ni and Mo plates were ultrasonically washed by 2-propanol followed by the overnight immersion into 2-propanol. In the case of the formation of surface monolayer films on Au, Ag and Cu, the cleaned metal

Table 1 XPS measurement condition

X-ray source	mono-Al K α
Power/Voltage	300 W/14.0 kV
Emission angle	45°
Analysis Region	O 1s, C 1s, F 1s, S 2p or Si 2p, X (X=Au 4f, Ag 3d, Cu 2p, Ni 2p, Mo 2p)
measurement time	3~4 hours

substrates were immersed into 1 mM PFDT/ethanol solution to form PFDT films on these surfaces. On the other hand, the cleaned Si, Ni and Mo plates were immersed into 1 mM PFDS/hexane solution to form PFDS film. After the surface modification, the substrates covered by PFDT thin film were rinsed with ethanol, and that covered by PFDS film were rinsed with hexane, ethanol and acetone, respectively. Then, samples were immediately inserted into the XPS chamber for measurements.

XPS MEASUREMENT

The XPS measurements of perfluorinated organic thin films prepared were performed by using a Physical Electronics PHI 5600ci spectrometer with monochromated Al K α X-ray source. The reason for using monochromatic source was that the factors of sample damage should be limited to the irradiation of X-ray and photoelectrons generated from the sample itself, *i.e.* heat radiation and electron beams from the Al filter can not be regarded. The power of X-ray source was 300W, the incident angle of X-ray was 45 degree and the emission angle (detection angle) from the surface normal was also 45 degrees.

The XPS measurements were carried out using profile mode without sputtering to obtain the change of peak intensity for 3-4 hours. Table 1 summarizes the XPS measurement condition. After sample damaging experiment, the Ag 3d_{5/2} peak of a silver plate sputtered with Ar ion was measured to calculate the relative X-ray dose, *D*. The conditions for sample damaging and silver plate measurements were exactly the same.

RESULTS AND DISCUSSION

The reaction schemes of PFDT and PFDS film formation on solid substrates are illustrated in Fig. 1.

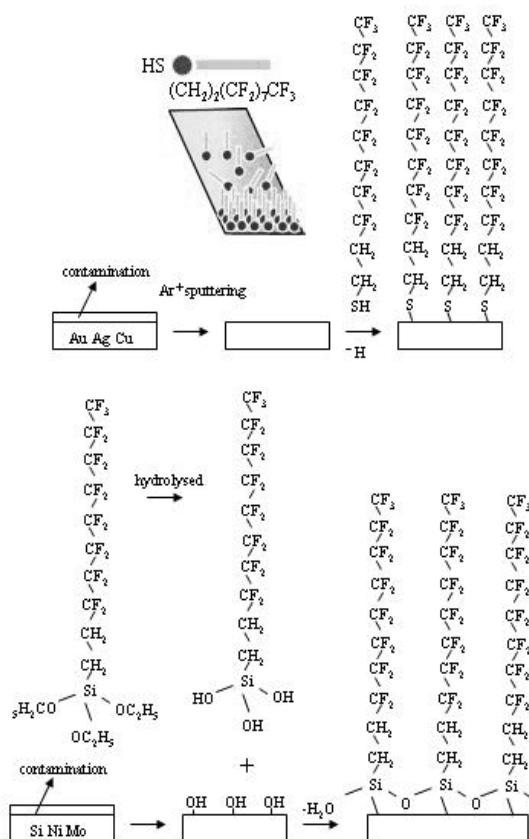


Fig. 1 The reaction schemes of PFDT film and PFDS film formation on the solid substrates

In the case of PFDT, the SH group of PFDT was chemically adsorbed on the bare metal surface. On the other hand, PFDS was firstly hydrolyzed by water adsorbed on the substrates, and condensation reaction occurs with surface hydroxyl groups, resulting in the formation of monolayer strongly combined with the substrate.

Figure 2 shows the changes of F 1s, C 1s, S 2p and Au 4f spectra of PFDT film on Au plate. The X-axis is the binding energy, Y-axis is the measurement cycle and Z-axis is the peak intensity. The C 1s region can be decomposed into three distinct peaks. The peaks of 293 eV, 291 eV and 285 eV are considered to be CF₃, CF₂ and CH₂ groups and/or the surface contaminants, respectively. The intensities of F 1s peak and CF₂ and CF₃ peaks in C 1s region drastically decrease with the measurement cycle. On the other hand, the intensities of CH₂ in C 1s and S 2p peaks are almost constant, and that of Au4f peak and CF (288eV) in C 1s slightly increase. Therefore the

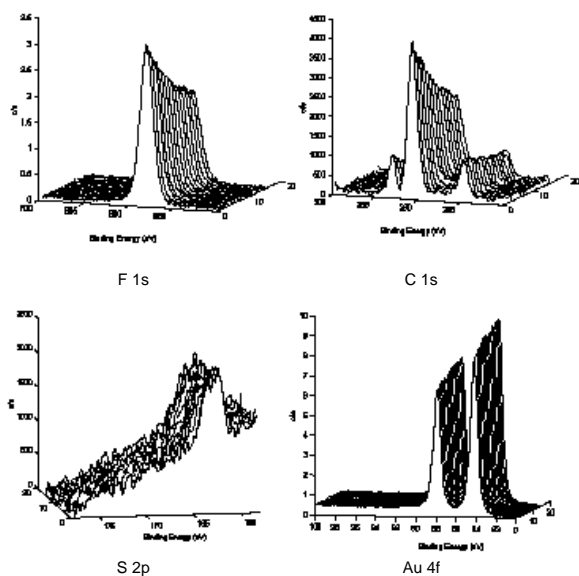


Fig. 2 The changes of F 1s, C 1s, S 2p and Au 4f spectra of PFDT film on Au plate

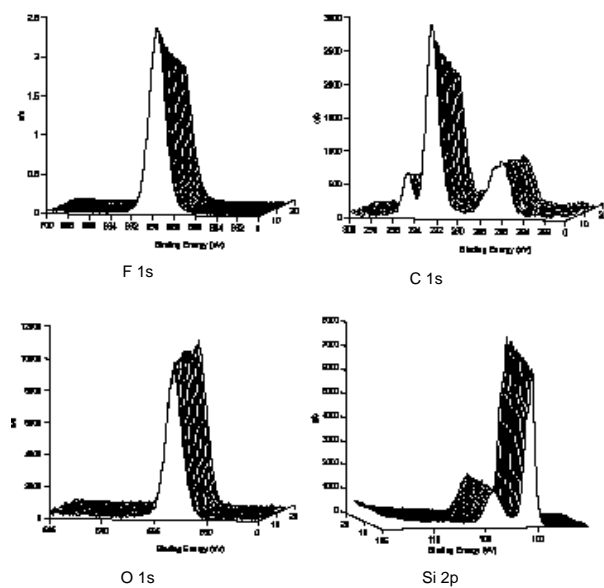


Fig. 3 The changes of F 1s, C 1s, O 1s and Si 2p spectra of PFDS film on Si wafer

degradation of PFDT film on Au plate mainly occurs in the scission of C-F bond during XPS measurement.

Figure 3 shows the changes of F 1s, C 1s, O 1s and Si 2p peaks of PFDS film on Si wafer. It has similar tendency of PFDT film on Au plate. Thus, the degradation mechanism of this film is considered to be similar as that of PFDT film.

PFDT films on Ag and Cu plates and PFDS films on Ni and Mo plates have also similar tendencies. So that, all of the perfluorinated organic thin films made in this study have the same manner of degradation.

Figure 4 shows the time course of F 1s peak intensity of PFDT film on Au substrate. It indicates the exponential decay.

This decay shape is similar to that of Cl 2p peak for the organic thin film made of chloropropyltriethoxysilane on silicon wafer substrate^[14]. Thus, the decay curve of F 1s peak intensity in Fig. 4 might be also evaluated by the following first order reaction equation.

$$\ln\left(\frac{I_{F1s}}{I_{F1s}^0}\right) = -\beta D \quad (1)$$

Where I_{F1s} is the peak intensity of F1s at time t , and I_{F1s}^0 is the initial one. D is the relative X-ray dose, which was calculated by multiplying measurement time and peak intensity of $Ag3d_{5/2}$ $D = I_{Ag}t$. β is the damaging factor of the prepared samples under the experiment condition. Comparing these values, the degradability for many substances might be evaluated under the same conditions.

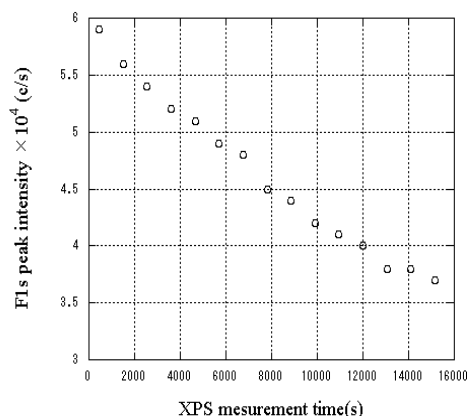


Fig. 4 Time course of F 1s peak intensity of PFDT film on Au substrate

Figure 5 shows the relationship between the natural logarithm of normalized peak intensity and D for all samples. The damaging factor β calculated

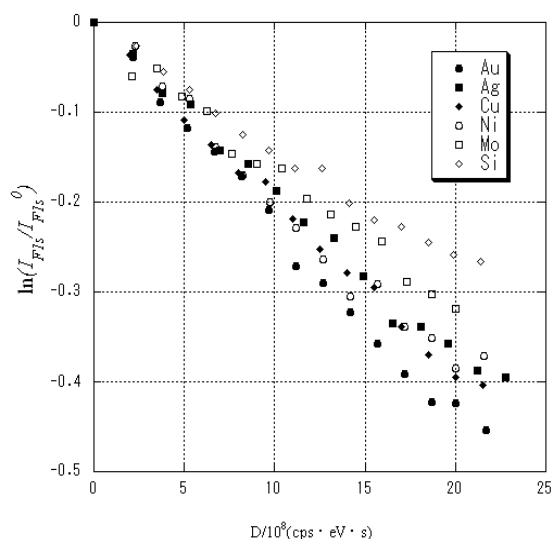


Fig. 5 Relationship between normalized peak intensity and D .

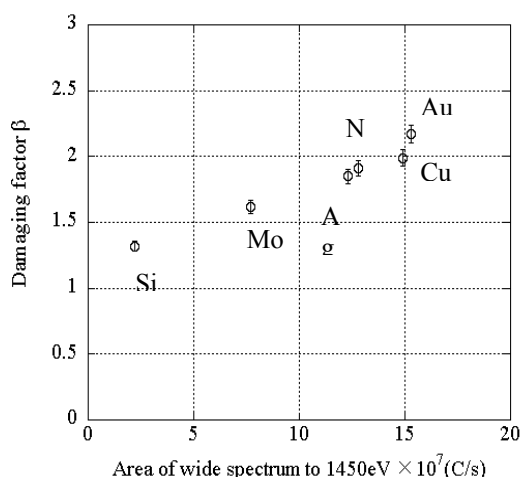


Fig. 6 Relationship between β and area of wide spectrum

from Eq. (1) is Au: $2.17 \times 10^{-10} \pm 0.05$, Cu: $1.96 \times 10^{-10} \pm 0.02$, Ag: $1.85 \times 10^{-10} \pm 0.02$, Ni: $1.91 \times 10^{-10} \pm 0.03$, Mo: $1.56 \times 10^{-10} \pm 0.04$ and Si: $1.38 \times 10^{-10} \pm 0.04$ ($\text{cps}^{-1} \text{eV}^{-1} \text{s}^{-1}$), respectively. Thus the degradation rates are in the order, Au > Cu > Ni > Ag > Mo > Si.

In the present study, we have focused on the photoelectrons generated from the sample itself, especially from the substrates used. If the sample damage is mainly caused by the emitted photoelectrons, the kinds of substrates will affect β values because the surface organic films used were very thin. That is, the β value depends on the amount

of photoelectrons generated inside the sample. Although the scission of C-F bond may occur mainly by lower energy electrons formed by the inelastic scattering of photoelectrons as well as Auger electrons from the sample itself because the bond dissociation energy of C-F bond was around 5eV, it is difficult to define the quantity of the lower energy electrons. Therefore, we assumed that the overall intensity of wide spectrum from 0 to 1450 eV (kinetic energy; 36 to 1487 eV) is proportional to the total electrons or especially the lower energy electrons which may be effective to the damage.

The areas of wide scan were Au: 15.3×10^7 , Ag: 12.3×10^7 , Cu: 14.9×10^7 , Ni: 12.7×10^7 , Mo: 7.78×10^7 and Si: 2.15×10^7 cps·eV, respectively. Thus, the order of the amounts of photoelectrons generated inside the sample is Au > Cu > Ni > Ag > Mo > Si.

Figure 6 shows the relationship between β and the area of wide spectrum. From this plot, it was confirmed that the β values increased with the amounts of photoelectrons for the degradation of PFDT and PFDS thin films on substrates.

CONCLUSIONS

We observed the sample damage of perfluorinated organic thin films of PFDT on Au, Ag and Cu, and of PFDS on Ni, Mo and Si during XPS measurement. The first order reaction mechanism could be applied to the degradation of those films. The order of the damaging factor, β , was Au > Cu > Ni > Ag > Mo > Si. Assuming that the area of wide spectrum measured 0 to 1450 eV (kinetic energy; 36 to 1487 eV) was proportional to the total amounts of photoelectrons from the sample, the affect of photoelectrons generated from the sample on the degradation of perfluorinated organic thin film was clarified. It was found that β value increases with the amount of photoelectrons generated from the sample itself, especially from the substrates used.

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